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(54) Title: COMPOSITE PANELS FOR PROTECTION AGAINST RIFLE BULLETS

(57) Abstract

A ballistic protection composite panel is disclosed having multiple layers of fabric woven from heat stable yarns with high tenacity and impregnated by heat meltable matrix resin. The layers are molded together to form a single panel capable of withstanding high powered rifle bullets.

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TITLE

COMPOSITE PANELS FOR PROTECTION AGAINST RIFLE BULLETS

BACKGROUND OF THE INVENTION

High powered rifles are important threats to lives of soldiers and policemen due to the high energy of bullets fired from such rifles. Traditional protection against bullets, such as the 7.62 x 51 NATO Ball, included ceramic plates backed by resin impregnated high strength fiber. Disadvantages of such systems have been relatively high panel weight required for adequate protection and the likely propagation of damage on impact, thus affecting its ability to protect from multiple hits.

Recently, composite plates based on ultra-high-molecular-weight polyethylene fiber (UHMWPE) have been introduced. These plates are based on uni-directional structures of fiber and are effective for selected rifle threats. Disadvantages of these composite plates are that: a high investment is required for making uni-directional structures; the lay-up process is labor intensive and subject to error; a large thickness of structure is necessary due to the low density of the polyethylene fibers; the plates are unsuitable for high temperature applications; and the structures often suffer delamination after impact.

Other ballistic resistant compositions are known for use in protective garments wherein multiple layers of matrix impregnated fabric are stacked separately to maintain flexibility and a degree of comfort to the garment wearer. Disadvantages of these compositions are that they are for protection from low energy bullets and they are less efficient on a weight-for-degree-of-protection basis.

SUMMARY OF THE INVENTION

This invention relates to a molded composite panel for protection against high-energy rifle bullets which comprises a woven fabric made from heat stable yarns having a tenacity greater than 3550 MPa (28.0 grams per denier) and a heat meltable matrix resin material, impregnating the fabric layers and adhering the fabric layers together. The molded composite panel of this invention meets the requirements for Protection Level III in NIJ Standard 0103.01 or its foreign equivalents at an areal density of less than 28 kg/m^2.

The invention also relates to a process for making the above-mentioned composite panel comprising the steps of stacking layers of woven polyaramid fabric having an areal density of less than 400 g/m^2 and made from yarns having a tenacity greater than 3550 MPa with heat meltable matrix resin material and applying heat and pressure to mold the fabric with the matrix resin.

DESCRIPTION OF THE INVENTION

To obtain adequate protection from high powered rifle bullets, at an acceptable weight and thickness, has been a long term object of the ballistic protection art. The composite panel of this invention represents a significant advance in meeting that object as evidenced in tests performed in accordance with various industry standards and as described in the Examples set out herein below.

This invention is a composite panel molded from a heat meltable matrix resin material and a woven fabric. Specifically, this invention is a molded composite panel made from especially high tenacity, heat stable, yarns woven into fabrics which are laminated with heat meltable matrix resin material.

It has been discovered that such molded composite panels made using heat stable fibers of especially high tenacities, can be made into hard ballistic composite panels and will stop high energy

rifle bullets at an improved weight/performance ratio. Meaning that, as a result of this invention, molded composite panels of high tenacity yarns exhibit better bullet protection at lower weight than molded composite panels of lower tenacity yarns.

An important feature of the present invention is the use of especially high tenacity, heat stable, yarns in a light weight fabric. The tenacity of the yarns used in these fabrics is from 3550 MPa (28.0 grams per denier) to 5760 MPA (45.0 grams per denier) and preferably greater than 3675 MPa (29.0 grams per denier). By "heat stable" is meant that the yarns and fibers in the yarns melt or decompose at a temperature greater than 200°C.

Yarns of this invention can be made using any material which exhibits adequate tenacity and heat stability. They must, of course, be capable of being woven and processed at the temperatures required for molding the composite panels. Among such materials can be named polyaramids, polybenzoxazoles, polybenzothiazoles, and the like.

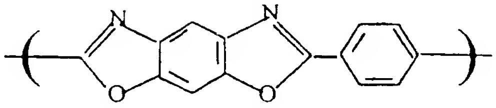
When the yarns are polyaramid, by "polyaramid" is meant a polyamide wherein at least 85% of the amide (-CO-NH-) linkages are attached directly to two aromatic rings. Suitable polyaramid fibers are described in Man-Made Fibers - Science and Technology, Volume 2, Section titled Fiber-Forming Aromatic Polyamides, page 297, W. Black et al., Interscience Publishers, 1968. POlyaramid fibers are, also, disclosed in U.S. Patents 4,172,938; 3,869,429; 3,819,587; 3,673,143; 3,354,127; and 3,094,511.

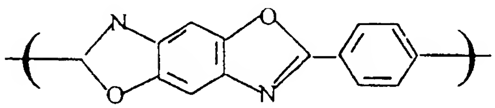
Additives can be used with the polyaramid and it has been found that up to as much as 10 percent, by weight, of other polymeric material can be blended with the polyaramid or that copolymers can be used having as much as 10 percent of other diamine substituted for the diamine of the polyaramid or as much as 10 percent of

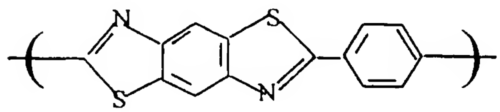
other diacid chloride substituted for the diacid chloride or the polyaramid.

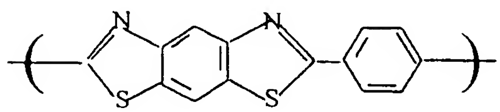
The preferred polyaramid is a para-aramid and poly(p-phenylene terephthalamide)(PPDT) is the preferred para-aramid. By PPDT is meant the homopolymer resulting from mole-for-mole polymerization of p-phenylene diamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other diamines with the p-phenylene diamine and of small amounts of other diacid chlorides with the terephthaloyl chloride. As a general rule, other diamines and other diacid chlorides can be used in amounts up to as much as about 10 mole percent of the p-phenylene diamine or the terephthaloyl chloride, or perhaps slightly higher, provided only that the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction. PPD-T, also, means copolymers resulting from incorporation of other aromatic diamines and other aromatic diacid chlorides such as, for example, 2,6-naphthaloyl chloride or chloro- or dichloroterephthaloyl chloride or 3,4'-diaminodiphenylether.

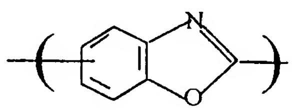
When the yarns are polybenzoxazoles or polybenzothiazoles, the polymers are preferably made up of mers of the following structures:

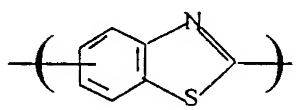












While the aromatic groups shown joined to the nitrogen atoms may be heterocyclic, they are preferably carbocyclic; and while they may be fused or unfused polycyclic systems, they are preferably single six-membered rings. While the group shown in the main chain of the bis-azoles is the preferred para-phenylene group, that group may be replaced by any divalent organic group which doesn't interfere with preparation of the polymer, or no group at all. For example, that group may be aliphatic up to twelve carbon atoms, tolylene, biphenylene, bis-phenylene ether, and the like.

The polybenzoxazole and polybenzothiazole used to make fibers of this invention should have at least 25 and preferably at least 100 mer units. Preparation of the polymers and spinning of those polymers is disclosed in the aforementioned International Publication WO 93/20400.

The fabrics are woven and can be woven in any, generally-used fabric configuration such as plain weave, crowfoot weave, basket weave, satin weave, and the like. Plain weave is preferred.

The areal density of fabrics used in this invention is less than 400 g/m^2; preferably less than 200 g/m^2, more preferably less than 160 g/m^2 and most preferably less than 120 g/m^2.

The matrix resin used in the composite panel of this invention is a thermoset, an elastomer, or a thermoplastic. All matrix resins must, of course, be at least, initially heat meltable for manufacture of the molded composite panel of this invention. Thermoplastic matrix resins are preferred. The role of the matrix resin is to hold individual fibers and yarns in place in each fabric layer and to adhere together adjacent fabric layers in the panel.

Examples of thermoset matrix resins include unsaturated polyester resins, epoxy resins, phenol resins, melamine resins, urea resins and a reacted mixture of phenol and poly(vinyl butyral) resins, and the like. The reacted mixture of phenol and poly(vinyl butyral) is preferred.

Examples of elastomeric matrix resins are summarized in the Encyclopedia of Polymer Science, Vol 5, "Elastomers Synthetic" (John Wiley & Sons 1964). For example, any of the following materials may be employed: polybutadiene, polyisoprene, ethylene-propylene copolymers, polyurethane elastomers, polyethers, polyesters, fluorelastomers, silicone elastomers, thermoplastic elastomers and the like. Thermoplastic elastomers are preferred.

Examples of thermoplastic matrix resins are low density polyethylene, polyamides, ionomers, polyesters, and the like. Low density polyethylene is preferred for most applications.

Matrix resins can be chosen to melt at a particular processing temperature to permit molding of temperature sensitive fabrics.

Matrix resin should be present in an amount which will completely impregnate the fabric of the panels. Too little matrix resin will cause poor consolidation of the molded composite panel and too much will adversely affect the ballistic protection limit of the molded panel. The composite panels of this invention should be 5 to 50 weight percent matrix resin, more preferred is 5 to 30 weight percent matrix resin and most preferred is 8 to 18 weight percent matrix resin.

In manufacture of the composite panels, the fabric is cut into layers of the desired shape and sizes and then the layers are stacked together with a matrix resin material. Generally, the layers are alternating fabric and matrix resin material and, generally, the matrix resin material is a film or a coating on the fabric. The layers are then molded, by the application of heat and pressure, to make a hard ballistic panel.

The areal density of the molded composite panel of this invention is less than 28 kg/m^2 to meet Protection Level III in NIJ (National Institute of Justice) Standard 0103.01 or its foreign equivalents such as the UK RF1 Level, as specified by UK Police Scientific Development Branch (PSDB) Body Armour Standard 1995. More preferred areal density is less than 25 kg/m^2 to meet the aforementioned protection level and most preferred areal density is less than 22.5 kg/m^2.

The process of this invention saves considerable labor cost during panel making compared

with the uni-directional process. In addition, the composite of this invention can be made by persons having conventional weaving equipment and processes without additional investment in expensive uni-directional machinery.

TEST METHODS

Linear Density. The linear density of a yarn is determined by weighing a known length of the yarn. "denier" is defined as the weight, in grams, of 9,000 meters of the yarn; and "dtex" is defined as the weight, in grams, of 10,000 meters of the yarn.

In actual practice, the measured denier or dtex of a yarn sample, test conditions, and sample identification are fed into a computer before the start of a test; the computer records the load-elongation curve of the yarn as it is broken and then calculates the properties.

Tensile Properties. Yarns tested for tensile properties are, first, conditioned and, then, twisted to a twist multiplier of 1.1. The twist multiplier (TM) of a yarn is defined as:

$$TM = (turns/cm)(dtex)^{1/2}/30.3$$

The yarns to be tested are conditioned at 25°C, 55% relative humidity for a minimum of 14 hours and the tensile tests are conducted at those conditions. Tenacity (breaking tenacity), elongation to break, and modulus are determined by breaking test yarns on an Instron tester (Instron Engineering Corp., Canton, Mass.).

Tenacity, elongation, and initial modulus, as defined in ASTM D2101-1985, are determined using yarn gage lengths of 25.4 cm and an elongation rate of 50% strain/minute. The modulus is calculated from the slope of the stress-strain curve at 1% strain and is equal to the stress in grams at 1% strain (absolute) times 100, divided by the test yarn linear density.

Ballistics Performance. Two types of ballistic tests were performed in the context of this invention: (i) Ballistic Limit (V_{50}) and (ii) Certification (V_0) types of testing in accordance with a ballistic specification. The objective of Ballistic Limit (V_{50}) tests is to compare the relative performance of different materials against a selected projectile. The objective of Certification tests (V_0) is to demonstrate that, having achieved the Ballistic Limit (V_{50}) required, the system under test can withstand the shootings in accordance with the particular shooting sequence and pattern, as specified in the test. The shooting sequence and pattern are described in specific examples.

Ballistic tests of multi-layer panels are conducted to determine the ballistic limit (V_{50}) in accordance with a variation of the NATO Standard (Stanag 2920 - Ballistic Test Method for Personal Armours), generally, as follows: A panel to be tested is placed against a backing material of Roma Plastina No. 1 clay in a sample mount to hold the panel perpendicular to the path of test projectiles. The projectiles are propelled from a test barrel capable of firing the projectiles at different velocities. The first firing for each panel is for a projectile velocity estimated to be the likely ballistics limit (V_{50}). When the first firing yields a complete panel penetration, the next firing is for a projectile velocity of about 30 meters (98 feet) per second less in order to obtain a partial penetration of the panel. On the other hand, when the first firing yields no penetration or partial penetration, the next firing is for a velocity of about 30 meters (98 feet) per second more in order to obtain a complete penetration. After obtaining one partial and one complete projectile penetration, subsequent velocity increases or decreases of about 15 meters (49 feet) per second are used until

enough firings are made to determine the ballistics limit (V_{50}) for that panel.

The ballistics limit (V_{50}) is calculated by finding the arithmetic mean of an equal number of at least two of the highest partial penetration impact velocities and the lowest complete penetration impact velocities, provided that there is a difference of not more than 40 meters (131 feet) per second between the highest and lowest individual impact velocities.

EXAMPLES

Example 1

Three composite panels were made using fabrics woven from three different para-aramid yarns as shown below. The fabrics were in a plain weave and had an areal density of 185 - 190 grams per square meter.

Yarn	Tenacity	Modulus
A	28.9 gpd	736 gpd
B	26.5	760
C	26.5	570

All of the yarns were 840 denier with 560 filaments, were made from poly(p-phenylene terephthalamide) and were available from E. I. du Pont de Nemours and Company under the following tradenames: A - Kevlar Fiber Type NFT; B - Kevlar Fiber Type 964C; and C - Kevlar Fiber Type 964H.

To make the panels using each fabric, 110 pieces of fabric 25x30 centimeters were cut and stacked, alternating with sheets of linear low density polyethylene film having a thickness of 0.02 mm for a matrix resin. Each stack was molded at a pressure of 40 to 60 bars and 150 degrees C for at least 20 minutes and was then cooled and trimmed to make a panel. The panels had 14 weight percent matrix resin and areal densities of 25.5 to 25.7 kilograms per square meter. Each panel was tested for V_{50} Ballistic Performance

using an 0.308 Winchester (7.62x51 NATO Ball, Norma - 17622) against a Roma Plastilina No. 1 backing block conditioned in accordance with NIJ Standard 0103.01.

V_{50} results were as follow:

Panel fabric	V_{50} (m/s)
A (Invention)	842.6
B (Comparison)	818.6
C (Comparison)	796.4

Note that panels made using fabrics B and C do not represent panels of this invention and were tested for comparison purposes.

Example 2

Three composite panels were made using fabrics woven from two different high tenacity yarns as shown below. The fabrics were in a plain weave and had an areal density of 185 grams per square meter.

Yarn	Tenacity	Modulus
D	40-43.5 gpd	1380-1390gpd
E	27.0	781

Yarn D was made from a poly(p-phenylene 2,6-benxobisoxazole) (PBO) and was available from Toyobo Co., Ltd under the tradename of Zylon; and yarn E was made from poly(p-phenylene terephthalamide) (PPDT) and was available from E. I. du Pont de Nemours and Company under the tradename of Kevlar 964C. Each yarn had about 667 filaments and a denier of 1000.

To make the panels using these fabrics, 115 pieces of fabric 25x30 centimeters were cut and stacked, alternating with sheets of linear low density polyethylene film having a thickness of 0.020 mm for a matrix resin. Three panels were made. One each using 100% of one of the fabrics and one using 50% of each of

the fabrics. The different fabrics were alternated in the panel using 50% of each of the fabrics. Each stack was molded under the same conditions as were used in Example 1 and then was cooled and trimmed to make a panel. The panels had 14-15 weight percent matrix resin and areal densities of 26.8 to 26.9 kilograms per square meter. Each panel was tested in the same way and under the same conditions as were used in Example 1.

V_{50} results were as follow:

Panel fabric	V_{50} (m/s)
100% PBT	911.8
50%/50% PBT/PPDT	897.7
100% PPDT	838.5

Note that the panel using 100% PPDT does not represent a panel of this invention and was tested for comparison purposes.

Example 3

A molded composite panel was made by stacking 122 layers of a plain weave woven fabric alternately with layers of linear low density polyethylene as a matrix resin and then subjecting the stack to a pressure of 40 bars at 150 degrees C for a period of 40-50 minutes. The fabric was made using yarns of PPDT having a denier of 600 and a tenacity of 28.1 grams per denier, available from E. I. du Pont de Nemours and Company under the tradename Kevlar A-200. The fabric had an areal density of 160 grams per square meter. The matrix resin, before molding, was in the form of film with an areal density of 20 to 22 grams per square meter. The composite panel had an areal density of 22 kilograms per square meter.

The panel was tested in accordance with the procedure of the United Kingdom, PSDB Hand-Gun Level II

using a NATO 7.62x51 L2A2 UK origin bullet. The panel was tested before a backing block of Roma Plastilina No. 1 conditioned in accordance with UK PSDB Ballistic Body Armour Standard (1995). The tests were carried out by firing three rounds of the specified bullet from a barrel capable of firing the projectiles at different velocities. In this case, the allowed velocities for "Fair Shots" fell within the range of 830 ± 15 m/s. The three shots were fired with a pattern of triangle, of which the distance between each shots was at least 100 mm. The results were as follow:

Velocity (m/s)	Penetration
827.1	No
823.7	No
821.7	No

These results indicate that this panel meets the Protection Level RF1 requirements set by UK PSDB Body Armour Standard (1995) at 22 kilograms per square meter. As a comparison, a traditional ceramic plate backed by a high strength fiber would require 30 -32 kg/m^2 to meet these requirements.

Example 4

The panel of Example 3 was tested as an insert panel for a soft vest designed to meet NIJ Standard 0103.01, protection level III. A NATO 7.62x51 Ball SMI (Italian origin) was used as the bullet. Shooting was carried out with a NATO Standard Issue 7.62 Calibre rifle capable of delivering projectiles at velocities at 838 ± 15 m/s. Three shots were fired following a pattern of a triangle, of which the distance between two shots was at least 100 mm. The results were as follow:

Velocity (m/s)	Penetration
834.7	No
843.2	No

845.3	No

Example 5

Panels having the same composition as Panel A from Example 1 were tested as insert plates for various soft vests under various testing methods. The panels had areal densities of 24.4 to 25.5 kilograms per square meter.

I. Testing in conjunction with a UK PSDB certified HG2 Level soft vest having an areal density of 7.7 kg/m^2 using a test method in accordance with the UK PSDB Ballistic Body Armour Standard (1995) for RF1 Protection Level with NATO 7.62x51 Ball L2A2 (UK origin) bullets

Velocity (m/s)	Penetration	Trauma (mm)
841	No	15
839	No	25
826	No	24

II. Testing in conjunction with a UK PSDB HG2 Level soft vest having an areal density of 12.1 kg/m^2 using a test method in accordance with the UK PSDB Ballistic Body Armour Standard (1995) for RF1 Level and for SG1 Level with NATO 7.62x51 Ball L2A2 (UK origin) bullets and 12-gauge 1 oz. Rifled Slugs, respectively.

Velocity (m/s)	Penetration	Trauma (mm)

For RF1 Level with NATO 7.62x51 Ball L2A2 bullets --

849	No	13
843	No	6
845	No	11

For SG1 Level with 12-gauge 1 oz. Rifled slugs -

444	No	0

III. Testing in conjunction with a soft vest under NIJ Standard Protection Level IIIA having an areal density of 6.6 kg/m^2 using a test method in accordance with NIJ Standard 0103.01 Protection Level III with NATO 7.62x51 Ball (M80 at 150 grains). The distance between each two shots should be at least 100 mm.

	Velocity (m/s)	Penetration	Trauma (mm)
First Panel			
	853	No	29
	855	No	
	858	No	
	852	No	
	854	No	33
	847	No	
Second Panel			
	853	No	33
	843	No	
	848	No	
	852	No	
	855	No	31
	850	No	

What is Claimed is:

1. A molded composite panel comprising multiple layers of a woven fabric made from yarns having a tenacity greater than 3550 MPa (28.0 grams per denier) wherein the fabric layers are impregnated with, and the multiple layers are adhered together by, a heat meltable matrix resin.

2. The composite panel of Claim 1 wherein the areal density of the panel is less than 28 kg/m^2.

3. The composite panel of Claim 1 wherein the panel meets the requirements for Protection Level III in NIJ Standard 0103.01 at an areal density of less than 28 kg/m^2.

4. The composite panel of Claim 1 wherein the heat meltable matrix resin is thermoplastic.

5. The composite panel of Claim 1 wherein the yarns have a tenacity of from 3550 MPa (28.0 grams per denier) to 5760 MPa (45.0 grams per denier).

6. The composite panel of Claim 1 wherein the thermoplastic matrix resin is polyethylene.

7. The composite panel of Claim 1 wherein the thermoplastic matrix resin is 5 to 50 weight percent of the total panel weight.

8. The composite panel of Claim 1 wherein the yarns are selected from polyaramid yarns, aromatic polybenzoxazole yarns, aromatic polybenzothiazole yarns, and combinations of those yarns.

9. The composite panel of Claim 1 wherein the yarns are poly(p-phenylene terephthalamide) yarns.

10. The composite panel of Claim 1 wherein the yarns are poly(p-phenylene 2,6-benzobisoxazole) yarns.

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(57) Abstract

A ballistic protection composite panel is disclosed having multiple layers of fabric woven from heat stable yarns with high tenacity and impregnated by heat meltable matrix resin. The layers are molded together to form a single panel capable of withstanding high powered rifle bullets. The yarns may be selected from polyamid (poly(p-phenylene terephthalamide)) yarns, polybenzoxazole yarns or polybenzothiazole yarns. The matrix resin may consist of thermoplastic polyethylene. The tenacity is greater than 3550 MPa (28.0 grams per denier).

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INTERNATIONAL SEARCH REPORT

Interr nal Application No
PCT/US 99/08235

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 F41H5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 F41H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 89 06190 A (ALLIED-SIGNAL) 13 July 1989 (1989-07-13) page 7, line 2 - line 37; claims 1,9,20,25,35; example 5	1-8 9,10
Y A	US 4 726 922 A (COCHRAN ET AL.) 23 February 1988 (1988-02-23) example 4; table IV	9 1,5,8
Y	WO 97 49546 A (DSM) 31 December 1997 (1997-12-31) abstract	10
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search

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